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M99/420/H(2)M

MARKSCHEME

May 1999

CHEMISTRY

Higher Level

Paper 2

SECTION A

1. (a) $4\text{C(s)} + 4\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{C}_3\text{H}_7\text{COOH(l)}$ [1 mark]

Notes: Insist on correct state symbols

In (b), (c), and (d), omission of super and subscripts is **not** penalised.

- (b) $\Delta H_f^\circ(\text{rxn}) = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$ [1 mark]

Note: Give [1 mark] if subsequent working is correct.

$$\begin{aligned} -2183.5 \text{ kJ} &= [4(-393.5 \text{ kJ mol}^{-1}) + 4(-285.9 \text{ kJ mol}^{-1})] \\ &\quad - [1(\Delta H_f^\circ(\text{butanoic acid})) + 5(0.0 \text{ kJ mol}^{-1})] \end{aligned}$$
 [1 mark]

Note: Give [1 mark] for correct substitution.

$$-2183.5 \text{ kJ} = [(-1574 \text{ kJ}) + (-1143.6 \text{ kJ})] - [1(\Delta H_f^\circ) + 0.0 \text{ kJ}]$$

$$-2183.5 \text{ kJ} = [(-2717.6 \text{ kJ})] - [1(\Delta H_f^\circ)]$$

$$\Delta H_f^\circ = 2183.5 \text{ kJ} - 2717.6 \text{ kJ}$$

$$\Delta H_f^\circ = -534.1 \text{ kJ or kJ mol}^{-1}$$
 [1 mark]

Note: Relate (b) to equation in (a) even if (a) is wrong max [3 marks].

- (c) $\Delta S_f^\circ(\text{butanoic acid}) = \Delta S_{\text{(butanoic acid)}}^\circ - [4S_{\text{(C)}}^\circ + 4S_{\text{(H}_2\text{)}}^\circ + S_{\text{(O)}}^\circ]$ [1 mark]

$$= 226.3 \text{ J mol}^{-1} \text{ K}^{-1} - [4(5.7) + 4(130.6) + 1(205.0)] \text{ J mol}^{-1} \text{ K}^{-1}$$
 [1 mark]

$$= -523.9 \text{ J mol}^{-1} \text{ K}^{-1} \text{ OR } -0.5239 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
 [1 mark]

Note: Relate (c) to equation in (a), even if (a) is wrong

- (d) $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$ (may be assumed if answer correct) [1 mark]

$$= -534.1 \text{ kJ} - (298 \text{ K})(-0.5239 \text{ kJ K}^{-1})$$

$$= -378.0 \text{ kJ or kJ mol}^{-1}$$
 [1 mark]

Note: Answers to (b), (c) and (d) must be consistent with (a)

- (e) It is spontaneous since ΔG is negative Need all for [1 mark]

[Consequently, if in (d) ΔG is given as positive, then reaction is **not** spontaneous]

Total [10 marks]

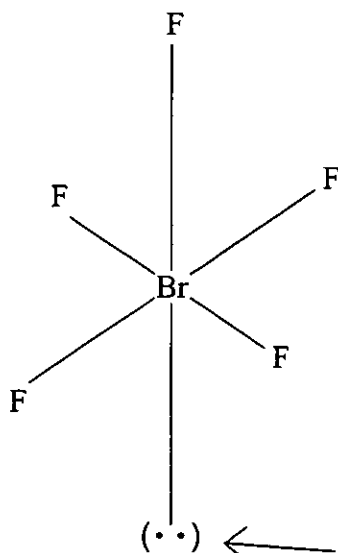
2. (a) (i) A solid (liquid not acceptable and high M_r not acceptable) [1 mark]
 Relatively large van der Waal's / intermolecular forces / H-bonding [1 mark]
 Note: Must have some discussion of bonding forces

- (ii) The large number of C-C and C-H bonds / the long non-polar chain outweighs the polar OH. [1 mark]
 [1 mark]

Allow [1 mark] for simply stating non-polar molecular

- (b) BF_3 has only three pairs of electrons about the central B atom. [1 mark]
 NF_3 has four pairs of electrons about the central N atom. [1 mark]
 or explanation in terms of sp^2/sp^3

- (c) Square pyramid [1 mark]



OR '(based on) octahedral' with suitable diagram: lone pairs must be there.

($\cdot\cdot$) ← not necessary for 'square pyramid' answer [1 mark]

- (d) one (sp) σ bond and two π bonds $\sigma/\pi = 1$ [1 mark]
 [1 mark]

Triple bond for 1 compensatory mark

$$2\sigma, 1\pi = 1$$

$$1\sigma, 1\pi = 1$$

if C_2H_4 , "double" = 0

$$1\sigma, 1\pi = 1$$

Total [10 marks]

3. (a) $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$ insist on [] [1 mark]

(b) (i) $[\text{NO}_2]$ increases or yield increases [1 mark]
 since $[\text{N}_2\text{O}_4]$ increases and K_c is constant [1 mark]

OR equilibrium moves to the right

(ii) $[\text{NO}_2]$ decreases or yield decreases [1 mark]
 since increased pressure pushes equilibrium to the left [1 mark]

OR by Le Chatelier's Principle the smaller volume is favoured

(iii) $[\text{NO}_2]$ unchanged or yield unchanged [1 mark]
 catalyst does not affect position of equilibrium [1 mark]

OR both forward and backward reaction rates affected equally

(c) (i) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ [1 mark]
 0.8 0.4

(ii) $\frac{(0.4)^2}{0.8} = 0.2 \text{ mol dm}^{-3}$ [2 marks]
 [1] [1]

Note: Carry forward error from (a) in both numerical answer and units
 Error carried forward in (c) (ii), e.g. if $[\text{NO}_2]$ is given as 0.2
 then $K_c = 0.05$

(d) K_c increased [1 mark]
 since forward reaction is endothermic [1 mark]

OR equilibrium moves to right as temperature increases

Total [14 marks]

4. (a) 2 [1 mark]

(b) 1 [1 mark]

(c) $\text{Rate} = k[\text{A}]^2[\text{B}]$ [] must be used [1 mark]

(d) $0.5 = k(0.2)^2(0.2)$ $k = 62.5$ error carried forward from (c) [1 mark]

Total [4 marks]

5. (a) Step 1 since it is the slowest. (Explanation must be given.) [1 mark]

(b) Step 1 [1 mark]
 Slowest step, therefore has a higher activation energy relative to Step 2. [1 mark]

(c) $\text{Rate} = k[\text{NO}_2][\text{F}_2]$ mark consequentially on (a) [1 mark]

Total [4 marks]

SECTION B

6. (a) s, p, d, f [2 marks]
 1 error, for example s, p, f, d or p, s, d, f deduct 1 mark
 p, s, f, d 0 marks

- (b) $d = 5, f = 7, p = 3, s = 1$ 4 correct [2 marks]
 2 or 3 correct [1 mark]
 1 correct [0 marks]

Any answer which suggests the above

- (c) Any 2 from 3:
 electrons move (to lower) energy levels/orbitals [1 mark]
 emitting energy as they do so [1 mark]
 excitation and/or promotion to higher energy level [1 mark]

- (d) Fill **singly before doubling** [1 mark]
 since two **electrons** in the same orbital will **repel**/Hund's rule/orbitals are degenerate [1 mark]
 $Ti\ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ or reversed or $Ar\ 3d^2 4s^2$ [1 mark]
 Note: Must be superscript: $1s^2$

- (e) (i) Order must be correct:
 Mass spectrometer. [1 mark]
 A sample of naturally occurring **gallium vapour** [1 mark]
 is injected into the evacuated ionising chamber where an **electron beam ionises a part of the sample** by knocking electrons from the neutral atoms or molecules. [1 mark]
Charged plates accelerate the positive ions towards the detector [1 mark]
 and the **ions pass through a magnetic field** perpendicular to their path [1 mark]
 where the charged ions are **separated (deflected) into different paths**. [1 mark]
 The **detector detects the paths according to the masses of the particles**. [1 mark]
 Accept labelled diagram and adequate explanation.

Any five points from the six given. [max 6 marks]

- (ii) Ga-69 31p 38n [1 mark]
 Ga-71 31p 40n [1 mark]

$$\frac{(60 \times 69) + (40 \times 71)}{100} \quad [1 \text{ mark}]$$

69.8 [1 mark]

continued...

Question 6 continued...

- (f) (i) **removed from a positively charged ion, $\text{Be}^+(\text{g})$, whereas** **[1 mark]**
the first electron is removed from a neutral atom, $\text{Be}(\text{g})$. **[1 mark]**

1st electron is removed from a full sub-orbital; 2nd electron is removed from a singly occupied sub-orbital, gains [1 mark] only

- (ii) Electron from 3p in Al but **[1 mark]**
 electron from 3s in Mg **[1 mark]**
 which is of lower energy

- (iii) Electron from 2(p) in B ('p' not essential)
 Electron from 3(p) in Al ('p' not essential) **[1 mark]**

The latter is further from the nucleus / the former is nearer to the nucleus

[1 mark]

Total [25 marks]

7. (a) (i) NaHCO_3 : Brønsted–Lowry base because proton acceptor, [1 mark]
 Lewis base because electron pair donor. [1 mark]
 CaCO_3 : Both [1 mark]

- (ii) $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$ [1 mark]
 OR $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

Note: If H_2CO_3 , no mark given.

- $\text{Al}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$ [2 marks]
 OR $\text{Al}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O}$
 OR $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3 + 3\text{H}^+ \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}$

Note: [1 mark] for correct species, [1 mark] for correct balance.



Note: If H_2CO_3 **again**, do not penalise.

- (iii) $n_{\text{mol}} \text{NaHCO}_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{84 \text{ g mol}^{-1}} = 0.012$ [1 mark]

$n_{\text{mol}} \text{Al}(\text{OH})_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{78 \text{ g mol}^{-1}} = 0.013$ [1 mark]

$n_{\text{mol}} \text{CaCO}_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{100 \text{ g mol}^{-1}} = 0.010$ [1 mark]

$\text{Al}(\text{OH})_3$ reacts with 3 mol of H^+ so it is more effective than
 CaCO_3 which reacts with 2 mol of H^+ which is more effective than
 NaHCO_3 which reacts with 1 mol of H^+

[3 marks]

- OR $\text{Al}(\text{OH})_3$ best [1 mark]
 CaCO_3 a further [2 marks] if stoichiometry [1 mark]
 NaHCO_3 worst has been used to explain the rest of the [1 mark]
 order

Note: If order is wrong look for consequential marking

- (iv) NaOH is a strong alkali [1 mark]
 damages body tissues / corrosive to body [1 mark]
 difficult to store

Note: Accept other answers on merit

continued...

Question 7 continued...

(b) (i) amphoteric/amphiprotic [1 mark]

(ii) $\text{Zn}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$ equation 1, balanced 1 [2 marks]

$\text{Zn}(\text{OH})_2 + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-}$ (OR $\text{ZnO}_2^{2-} + 2\text{H}_2\text{O}$) [2 marks]

$\text{Al}(\text{OH})_3$ / $\text{Pb}(\text{OH})_2$ / $\text{Sn}(\text{OH})_2$ / Al_2O_3 / $\text{Cr}(\text{OH})_3$ / accept other suitable oxides/hydroxides (not H_2O) [1 mark]

(iii) Electron pair acceptor. [1 mark]

They have available / empty (*d*) orbitals. [1 mark]

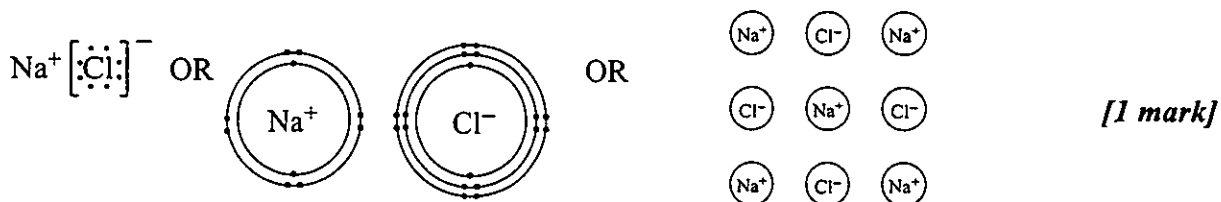
e.g. $\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$ [2 marks]

choice of base (ligand) 1, formula of suitable complex 1 Total [25 marks]

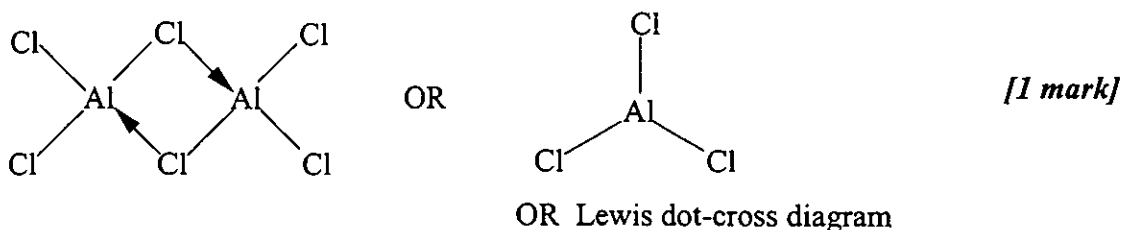
N.B. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, both are acceptable

Note: Equation does not have to be balanced

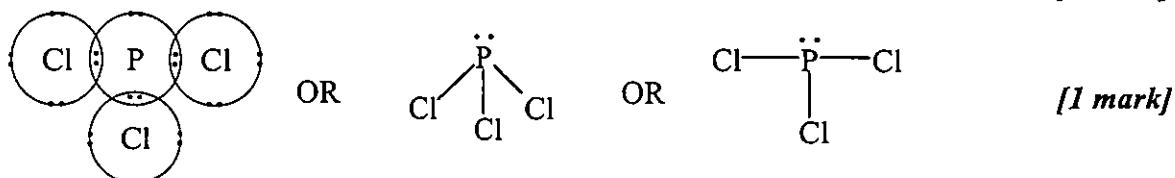
8. (a) (i) NaCl – high melting and boiling points – giant structure/ionic [1 mark]
 – strong attraction between ions [1 mark]



- Al_2Cl_6 – low melting and boiling points – simple molecular/covalent [1 mark]
 – associated or weak forces between individual molecules [1 mark]



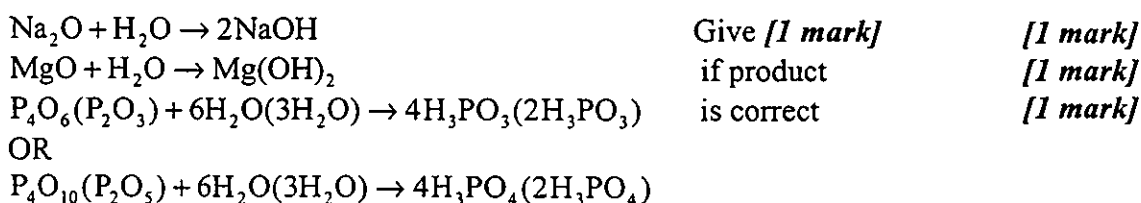
- PCl_3 – low melting and boiling points – simple molecular/covalent [1 mark]
 – weak forces between individual molecules [1 mark]



- (ii) NaCl dissolves (do not accept dissociates) [1 mark]
 AlCl_3 vigorous reaction /exothermic/fizzing/gas evolved [1 mark]
 PCl_3 gives vigorous reaction/exothermic/fizzing/gas evolved [1 mark]
 $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$ [1 mark]
 $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$ [1 mark]

- (b) (i) ionic, ionic, covalent, covalent [4 marks]

- (ii) strong alkali, weak alkali, nothing, acid [4 marks]
 OR OR OR OR
 high pH pH above 7 7 below 7



Total [25 marks]

9. (a) (i) $C_4H_{10}O = 74$ [1 mark]
Therefore molecular formula = $C_4H_{10}O$ [1 mark]
- (ii) Removal of $CH_3 / C_3H_7O^+$ is present [1 mark]
- (iii) OH [1 mark]
- (b) $CH_3CH_2CH_2CH_2OH$
- $$\begin{array}{c} CH_3-CH-CH_3 \\ | \\ CH_2OH \end{array}$$
 [2 marks]
- (c) (i) $C=C$ (or alkene) accept 'primary alcohol' or $-CH_2OH$ if candidate has misinterpreted the question [1 mark]
- (ii) $CH_3CH_2CH=CH_2$
$$\begin{array}{c} CH_3-C-CH_3 \\ || \\ CH_2 \end{array}$$
 [2 marks]
- (iii) $CH_3CH_2CH(Cl)CH_3$
 $CH_3CH_2CH_2CH_2Cl$
- $$\begin{array}{c} H \\ | \\ CH_3-C-CH_3 \\ | \\ CH_2Cl \end{array}$$

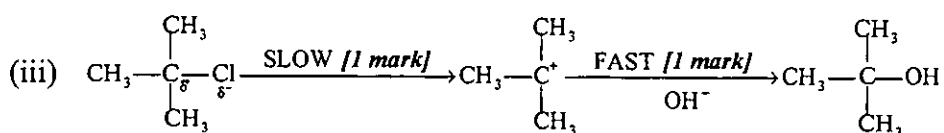
$$\left(\begin{array}{c} Cl \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \\ \text{given below so} \\ \text{no mark awarded} \end{array} \right)$$
 [3 marks]
- (d) CH_3-C-CH_3
 $||$
 CH_2 [1 mark]

The phrasing of the question may lead candidates to offer more than one answer. Give credit for correct answer – ignore the rest.

Question 9 continued...

- (e) (i) substitution [1 mark]
 nucleophilic [1 mark]
 1st order/unimolecular [1 mark]

- (ii) Steric effects of CH_3 [1 mark]
 CH_3 electron releasing [1 mark]
 The $(\text{CH}_3)_3\text{C}^+$ ion is stable [1 mark]



polarity
[1 mark]

[1 mark] OH^- ion + product [1 mark]

[5 marks]

Note: If candidate has given a lot of detail in (e)(i), carry forward credit to (e)(iii).

- (f) A tertiary alcohol cannot be oxidised. [1 mark]

Total [25 marks]